



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C04B 35/01, 35/10, 35/48, B32B 18/00, H01M 6/18		A1	(11) International Publication Number: WO 99/35104 (43) International Publication Date: 15 July 1999 (15.07.99)
<p>(21) International Application Number: PCT/US98/27859</p> <p>(22) International Filing Date: 31 December 1998 (31.12.98)</p> <p>(30) Priority Data: 09/002,483 2 January 1998 (02.01.98) US</p> <p>(71) Applicant (<i>for all designated States except US</i>): MATERIALS AND SYSTEMS RESEARCH, INC. [US/US]; 1473 Pioneer Road, Salt Lake City, UT 84104 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): VIRKAR, Anil, Vasudeo [US/US]; 1558 Devonshire Drive, Salt Lake City, UT 84108 (US). JUE, Jan-Fong [-/US]; 482 East Stonehedge Drive #4J, Salt Lake City, UT 84107 (US). FUNG, Kuan-Zong [-/US]; 2611 East 6600 South, Salt Lake City, UT 84121 (US).</p> <p>(74) Agent: SONNTAG, James, L.; P.O. Box 21, Heber City, UT 84032-0021 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: ALKALI-METAL-β-AND β''-ALUMINA AND GALLATE POLYCRYSTALLINE CERAMICS AND FABRICATION BY A VAPOR PHASE METHOD</p>			
<p>(57) Abstract</p> <p>A ceramic composite containing alkali-metal-β- or β''-alumina and an oxygen-ion conductor is fabricated by converting α-alumina to alkali-metal-β- or β''-alumina. A ceramic composite with continuous phases of α-alumina and the oxygen-ion conducting ceramic, such as zirconia, is exposed to a vapor containing an alkali-metal oxide, such as an oxide of sodium or potassium. Alkali metal ions diffuse through alkali-metal-β- or β''-alumina converted from α-alumina and oxygen ions diffuse through the oxygen-ion conducting ceramic to a reaction front where α-alumina is converted to alkali-metal-β- or β''-alumina. A stabilizer for alkali-metal-β''-alumina is preferably introduced into the α-alumina/oxygen-ion conductor composite or introduced into the vapor used to convert the α-alumina to an alkali-metal-β''-alumina.</p>			

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TITLE

ALKALI-METAL- β - AND β'' -ALUMINA AND GALLATE
POLYCRYSTALLINE CERAMICS AND FABRICATION BY A
VAPOR PHASE METHOD

5 FIELD OF THE INVENTION

This invention relates to the formation of polycrystalline alkali-metal- β - and β'' - alumina ceramics, particularly for use as electrolytes in sodium-sulfur batteries, alkali metal thermoelectric converters (AMTEC) and alkali metal sensors.

BACKGROUND OF THE INVENTION

10 One of the high-temperature secondary battery systems being investigated as a power source for electric vehicles is the sodium-sulfur battery. These batteries offer a high specific energy and high specific power, both of which are required for electric vehicles. These battery systems may also be potential energy storage devices for electric utilities, where long life and low cost are more important than high specific
15 energy and high specific power.

In a sodium-sulfur cell, a liquid anode of metallic sodium and liquid cathode of sulfur or sodium polysulfide are separated by a polycrystalline ceramic electrolyte of either sodium β - or β'' - Al_2O_3 . The operating temperature is typically between 300 and 400°C. In this battery, sodium ions diffuse during discharge from the anode to the
20 cathode by ionic conduction through the ceramic electrolyte. Usually the electrolyte is in the form of a tube with the liquid sodium anode in the interior of the tube. For high operating efficiency and low battery cost, it is essential that the conductivity of the electrolyte be as high as possible. For this reason, the preferred electrolyte is the sodium β'' - Al_2O_3 , because of its higher ionic conductivity.

25 The ceramic electrolyte is usually manufactured by mixing powders of Al_2O_3 and Na_2O (along with either Li_2O and/or MgO for stabilizing the β'' - phase) in appropriate proportions forming a powder compact and subjecting the powder compact to any one of various sintering processes. Examples of these processes are disclosed in "Sintering Processes and Heat Treatment Schedules for Conductive ,
30 Lithia-Stabilized β'' - Al_2O_3 " by G. E. Youngblood, A. V. Virkar, W. R. Cannon, and

R. S. Gordon: *Bull Am. Ceram. Soc.*, 1977, **56**, 206, and "Materials for Advanced High Temperature Secondary Batteries" by J. E. Battles: *International Materials Reviews.*, **34**. 1. In most sintering processes the formation of a grain boundary liquid phase is essential. The liquid phase formation can enhance the sintering kinetics, but 5 results in a large grain size, which decreases the mechanical strength of the electrolyte. The liquid phase sintering also generates a residual NaAlO₂ phase along the grain boundaries. The phase can react with moisture and further reduce the mechanical integrity of the ceramic electrolyte.

In United States Patent 5,415,127 to Nicholson et al. and in "Formation and 10 characterization of Na- β'' -alumina single crystal films" by Aichun Tan, Chu Kun Kuo and Patrick S. Nicholson: *Solid State Ionics* 1993, **67**, 131 is disclosed a method for the formation of Na- β'' -Al₂O₃ single crystal films. These films, because of their optical properties, have potential in solid-state lasers, holography, signal and image processing, phosphor chemistry, and other optical devices. The process comprises 15 providing a single crystal substrate of alpha-alumina with an optically smooth surface parallel to a (001) crystal plane, and heating the substrate in the presence of a vapor containing Na₂O to react with the alumina and a stabilizing ion, such as lithium. The polished surface is required to form a single crystal. Otherwise a polycrystalline material is formed. The alumina is converted to Na- β'' -Al₂O₃ as it reacts with sodium 20 oxide from the vapor. After conversion to Na- β'' -Al₂O₃ on the surface, further conversion requires that the Na₂O in the form of ions be transported through the already formed Na- β'' -Al₂O₃ and react with the alumina at a reaction interface. This provides a slow moving reaction front moving through the substrate. The kinetics of 25 this process is rather sluggish. Disclosed is conversion of a 40 μm thickness at 1600°C in one hour. To convert a 0.5 mm thick electrolyte plate or tube for a battery electrolyte, several hundred hours at $\geq 1450^\circ\text{C}$ would be required. This long time of formation materially adds processing and equipment costs to the fabrication. The limiting step is believed to be the diffusion of oxygen ions through the converted Na- β'' -alumina material, since the only species that exhibits high mobility in Na- β'' -alumina is the sodium ion. To convert alumina into Na- β'' -alumina, both sodium and 30 oxygen are required, and the diffusion of oxygen through Na- β'' -alumina is very slow.

Materials analogous to Na- β -alumina and Na- β'' -alumina also have been found to be useful in various processes. For example, in "Potassium Beta"-Alumina Membranes" G. M. Grosbie and G. J. Tennenhouse: *Journal of the American Ceramic Society*, **65**, 187 is disclosed membranes of the potassium analogs, K- β -alumina and K- β'' -alumina, that are made by ion-exchanging the sodium materials. These potassium materials have potassium-ion conductivity and may be used where the potassium-ion conductivity is required.

Sodium and potassium- β -alumina and β'' -alumina materials are also used in applications other than for battery applications, such as for sodium heat engines (SHE) or in general alkali-metal thermoelectric converters (AMTEC). Because of the continuing interest in these and the above battery technologies, a method for quickly producing electrolytes and other shapes without the disadvantages of sintered shapes would be an advance in the art.

Objects of the Invention

It is, therefore, an object of the invention to provide a method for forming alkali-metal- β - and β'' -alumina and gallate materials that do not require sintering and that avoids the formation of increased grain size and of grain boundary liquid phase.

Another object of the invention is to provide a method for forming alkali-metal- β - and β'' -alumina and gallate materials by diffusion wherein oxygen diffusion is accelerated and is not the limiting step.

Another object of the invention is to provide a method shortening the processing time in the formation alkali-metal- β - and β'' -alumina and gallate products by diffusion.

Further objects of the invention will become evident in the description below.

25 BRIEF SUMMARY OF THE INVENTION

The present invention is a composition and method for forming for alkali-metal- β - and β'' -alumina and gallate products. The method of the invention allows conversion of α -alumina into an alkali-metal- β - or β'' -alumina at a rate which is ten to hundred times larger than diffusion methods as disclosed in the Nicholson et al. patent.

The invention also involves the production of alkali-metal- β - or β'' -gallate from gallium oxide, Ga_2O_3 . Gallium has an analogous chemistry to aluminum as it applies to the present invention and composites of the invention can be made from α - Al_2O_3 or Ga_2O_3 , or mixtures thereof. Accordingly, it is understood that any disclosure 5 of the present invention for the production of alkali-metal- β - or β'' -alumina from α -alumina also applies to the production of alkali-metal- β - or β'' -gallate from gallium oxide. Mixtures of α - Al_2O_3 and Ga_2O_3 in the initial precursor composite, in which case a mixture of alkali-metal- β - or β'' - Al_2O_3 and alkali-metal- β - or β'' - Ga_2O_3 is formed, usually as a solution of the two.

10 The method of the invention comprises making a composite of α -alumina and an oxygen-ion conductor, such as zirconia, and then exposing it to a vapor containing an alkali-metal oxide, preferably an oxide of potassium or sodium, more preferably an oxide of sodium. The alkali-metal- β - or β'' -alumina may be of any of the alkali metals, including rubidium (Rb), cesium (Cs), and lithium (Li), but preferably sodium 15 (Na) and potassium (K), more preferably sodium (Na).

15 The vapor may also contain one or more stabilizers to inhibit transformation of β'' -alumina to the β -alumina. These include, but are not limited to MgO , Li_2O and ZnO . Other suitable stabilizer for β'' -alumina or β -alumina may also be added. Alternately, one or more stabilizers may be included in the formation of the α -alumina/oxygen-ion conductor composite.

20 The oxygen-ion conductor may be any suitable ceramic oxygen-ion-conducting material. Examples include, but are not limited to known oxygen-ion conductors, such as zirconia and its various forms, e.g., yttria stabilized zirconia, rare-earth-oxide-doped zirconia, and scandia-doped zirconia, and ceria ceramics, e.g., rare-earth doped ceria and alkaline-earth doped ceria, stabilized hafnia, and thoria.

25 The α -alumina and oxygen-ion conductor are formed into a ceramic composite by any conventional method for green forming, such as, for example, pressing, extrusion, slip casting, injection molding, tape casting, and the like, followed by sintering or hot-pressing. The physical properties of the final product derive in large 30 part from those of the initial ceramic composite. Accordingly, fabrication methods that produce high-strength, fine-grained materials are preferred.

Both, α -alumina and the oxygen-ion conductor are present in amounts to form continuous matrices of α -alumina phase and the oxygen-ion conductor phase. This provides two continuous, penetrating networks. Ceramic shapes of 30 to 70 vol.% α -alumina and 70 to 30 vol.% oxygen-ion conductor have been generally found suitable.

5 Shapes of a composition outside of these limits may also be suitable if a continuous matrix of both the α -alumina and oxygen conductor constituents is present.

The α -alumina/oxygen conductor ceramic shape is exposed to the appropriate ion species in the form of an alkali-metal-oxide at an elevated temperature, above about 800°C, preferably between 1200°C and 1500°C. If the temperature is too low,

10 the rate of reaction is inadequate. If the temperature is too high there can be an evaporation loss of the alkali-metal oxide. Additionally , it is also possible for alkali-metal- β'' -alumina to convert into alkali metal- β -alumina, especially above about 1600°C.

The vapor contains an oxide of the alkali-metal, preferably as Na₂O, if the

15 sodium form is desired, and potassium, preferably as K₂O, if the potassium form is required. The vapor also contains a stabilizing ion, preferably as Li₂O, MgO, ZnO if the β'' - form is desired. The process of the invention is preferably carried out by embedding the composite shape of α -alumina and oxygen-ion conductor in a powder that when heated to reaction temperature produces the appropriate vapor. For

20 example, a powder of alumina and alkali-metal- β or - β'' - alumina, or a powder of alumina and alkali-metal oxide calcined to form alkali-metal- β or - β'' - alumina is suitable. Any other suitable process for exposing the composite to alkali-metal vapors is contemplated.

During the process of the invention, oxygen ions transport through the

25 oxygen-ion conductor while sodium ions transport through the already formed alkali-metal- β - or β'' -alumina. In this manner, rapid paths are provided for both species and the reaction kinetics are not controlled by the rates of diffusion, but primarily by the formation of alkali-metal- β - or β'' -alumina at the reaction front; that is the boundary separating α -alumina (with oxygen-ion conductor) and formed alkali-metal- β - or β'' -

30 alumina (with oxygen-ion conductor).

The final product is a ceramic composite of the oxygen-ion conductor and the β -or β'' -alumina. Since no sintering conditions were required to form the β - or β'' -

alumina, there is no formation of liquid phases that compromise the properties of the composite. In addition, the oxygen-ion conductor can be chosen to contribute positively to the physical properties, providing a further enhancement.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Figure 1 is a schematic of a cross-section of an α -alumina and zirconia composite, showing the conversion process of α -alumina to sodium- β'' -alumina.

Figure 2 is a schematic of a cross-section of an α -alumina ceramic, showing a prior-art process.

10 Figure 3 is a plot of thickness converted, X vs. time, for various samples according to the invention and a comparative sample.

Figure 4 is an optical micrograph of a sample of a sodium- β'' -alumina/zirconia composite made according to the invention.

15 Figures 5A and 5B are respectively scanning electron micrographs of an α -alumina/zirconia sample, and the same sample after conversion of the α -alumina to sodium- β'' -alumina.

Figures 6 and 7 are respectively X-ray diffraction traces of an α -alumina/zirconia sample, and the same sample after conversion of the α -alumina to sodium- β'' -alumina.

20 Figure 8 is a plot of $\ln(\sigma T)$ vs. $1/T$ for a sample according to the invention.

Figure 9 is a plot of converted thickness squared vs. time of a sample according to the prior-art.

Figure 10 is a photomicrograph of the partially converted sample of the invention showing the interface between the K- β -alumina/8YSZ region and the α -alumina/8YSZ region.

25 Figure 11 shows a plot of the thickness vs. time for fabrication of a K- β -alumina/8YSZ composite of the invention.

Figure 12 shows a plot of $\ln(\rho/T)$ vs. $1/T$ for a K- β -alumina/8YSZ composite of the invention

DETAILED DESCRIPTION OF THE INVENTION

Compositions of the invention are made by first fabricating an α -alumina matrix with an added oxygen-ion conductor. The oxygen conductor may be any suitable oxygen conducting ceramic. The α -alumina and the oxygen conductor are present in an amount to provide a continuous matrix of both the α -alumina and the oxygen conductor phases.

Reference is made to Figure 1, which is a schematic of a cross-section of an α -alumina and an oxygen-ion conductor, zirconia, showing the conversion process of α -alumina to sodium- β'' -alumina. Shown is a composite of an α -alpha alumina phase 101 and an oxygen-ion conductor or zirconia phase 103. The α -alpha alumina phase is converted to sodium- β'' -alumina 105 along a reaction front 107. Sodium ions transport through the sodium- β'' -alumina 105 already converted from alumina, and oxygen ions transport through the zirconia 103. As the reaction proceeds, the reaction front advances and the thickness (X) of the converted α -alumina layer increases.

While only one surface is shown in Figure 1, it is understood that in an actual flat or cylindrical plate or film, conversion proceeds from both surfaces. The resulting material is a composite of sodium- β'' -alumina and the oxygen conductor.

Oxygen-ion conductors, such as zirconia, have good strength properties, and accordingly, the resulting composite is rather strong. By practice of the invention, the process of the invention produces dense composite ceramic particularly suitable for electrolytes.

As a comparison, reference is now made to Figure 2, which is a schematic that shows conversion of a pure α -alumina shape without an added oxygen conductor. In this process, both the sodium-ions and oxygen-ions must diffuse to the α -alumina phase 201 through the sodium- β'' -alumina 205 already converted from the α -alumina. Initially, Na_2O and Li_2O react with the surface $\alpha\text{-Al}_2\text{O}_3$ to form sodium- β'' -alumina. Further growth of sodium- β'' -alumina requires that Na_2O and Li_2O stabilizer be transported through the already formed sodium- β'' -alumina and to react with α -alumina at a reaction front at the sodium- β'' -alumina / $\alpha\text{-Al}_2\text{O}_3$ interface. The Na_2O diffusion occurs by the diffusion of both sodium and oxygen ions (shown by the arrows) through the already formed sodium- β'' -alumina to the reaction front 207. Since sodium- β'' -alumina is a sodium-conductor, diffusion of sodium-ions is rather

rapid. However, the diffusion of oxygen ions is much slower, by orders of magnitude. As a result, the rate of the α -alumina conversion is very slow because it is controlled mainly by the slow oxygen diffusion. This contrasts with the present invention, where both the sodium ions and the oxygen ions are quickly transported by rapid diffusion through the respective diffusion networks to the reaction front.

By practice of the present invention the conversion times are much shorter than the prior-art diffusion system, on the order of hours, as compared to days. This introduces a significant advantage into the conversion process.

Example I

Compositions of the invention were made using three different oxygen-ion conductors, (1) 8 mol.% Y_2O_3 -stabilized cubic phase zirconia (8YSZ), (2) 4.5 mol.% Y_2O_3 -stabilized tetragonal + cubic phase zirconia (4.5YSZ), and (3) rare earth oxide-doped ceria (CeO_2).

For the compositions made using zirconia, three types of discs were made: (a) 50 vol.% α -alumina + 50 vol.% 8YSZ, (b) 70 vol.% α -alumina + 30 vol.% 8YSZ, and (c) 50 vol.% α -alumina + 50 vol.% 4.5YSZ. Disc-shaped samples of 2.5 mm thickness of compositions (a), (b), and (c) were fabricated using requisite powder mixtures, die-pressing, followed by isostatic pressing, and then sintering in air at 1600°C. The discs after sintering were placed in a powder mixture containing Na_2O and Li_2O . The powder, having a composition; 8.85 wt.% Na_2O , 0.75 wt.% Li_2O , and 90.45 wt.% Al_2O_3 , was first calcined at 1250°C for 2 hours to form sodium- β "-alumina, and served as the source of sodium and lithium oxides during reaction. Samples were maintained at 1450°C for various periods of time ranging between 2 hours and 16 hours. The samples were cross-sectioned and the thickness of sodium- β "-alumina formed was measured.

Figure 3 shows a plot of the thickness measured as a function of time at 1450°C for three samples of the invention: (a) 50 vol.% α -alumina + 50 vol.% 8YSZ, (b) 70 vol.% α -alumina + 30 vol.% 8YSZ, (c) 50 vol.% α -alumina + 50 vol.% 4.5YSZ. Note that the thickness of the region converted into sodium- β "-alumina is in excess of 1500 μm (1.5 mm) for samples (a), (b), and (c) when heat-treated for 16 hours.

Figure 4 shows an optical micrograph (50 x magnification) of sample (b) after 8 hours at 1450°C in which the converted thickness is about 820 μm . Figure 5A shows a scanning electron micrograph (SEM) of the as-sintered sample (a) before conversion to sodium- β'' -alumina. The dark grains are those of α -alumina and the light ones are 8YSZ. Figure 5B shows an SEM micrograph of the same sample after converting α -alumina into Na- β'' -alumina. The dark grains are those of Na- β'' -alumina and the light ones are 8YSZ. Figure 6 is an X-ray diffraction (XRD) trace of an as-sintered, before-conversion, sample of composition (b) in which peaks corresponding to zirconia (labeled Z) and α -alumina labeled (α) can be seen. Figure 7 shows an XRD trace of the sample of composition (b) after heat treatment at 1450°C for 8 hours. The trace shows peaks corresponding to zirconia (labeled Z) and Na- β'' -alumina (unlabeled peaks). No peaks corresponding to α -alumina (α) can be seen.

A sample of composition (a) was heat-treated at 1450°C for a longer time (32 hours) to ensure that it was fully converted into Na- β'' -alumina all the way through. Conductivity, σ , was measured between 200 and 500°C. A plot of $\ln(\sigma T)$ vs. $1/T$ is shown in Figure 8. The activation energy was measured to be about 15.7 kJ/mol. Conductivity at 300°C was 0.0455 S/cm (resistivity of 22 Ωcm). This sample had 50 vol.% zirconia. Also, the grain size of Na- β'' -alumina was rather fine (a few microns). The measured σ was consistent with expected values for Na- β'' -alumina of a fine-grained structure.

Similar results with enhanced kinetics of conversion were also observed with ceria as the oxygen-ion conductor.

Example II

A composite of potassium- β -alumina and YSZ was fabricated according to the method of the present invention. A powder mixture containing 70 vol.% α -alumina and 30 vol.% 8YSZ was mixed in ethanol, dried, sieved and pressed into disc-shaped samples. The discs were sintered in air at 1600°C for 2 hours. Potassium- β -alumina powder containing K₂O: Al₂O₃ in 1:5 molar ratio was synthesized by calcining K₂O: Al₂O₃ powder in 1:5 molar ratio for 4 hours at 1250°C. The discs were embedded in the calcined K- β -alumina powder and the crucible was heated to 1450°C. Samples

were subjected to this heat treatment for 2 and 4 hours. XRD traces taken from the surface of the samples showed that the major phase was K- β -alumina. Figure 10 shows a photomicrograph of the partially converted sample showing the interface 301 between the K- β -alumina/8YSZ region 305 and the α -alumina/8YSZ region 303.

5 Figure 11 shows a plot of the thickness vs. time at 1450°C. Note that in 4 hours the thickness of the converted layer is about 1000 μm (1 mm). One disc was subjected to conversion heat treatment at 1450°C for 12 hours to ensure that the disc was fully converted. Ionic resistivity, ρ , was measured on this sample over a temperature range between 250 and 800°C. Figure 12 shows a plot of $\ln(\rho/T)$ vs. $1/T$ (T in °K). The activation energy was measured to be about 31.7 kJ/mol. The ionic resistivity, ρ , which is inverse conductivity, $1/\sigma$, at 800°C was about 38 Ωcm .

10

Example III

Compositions of the invention are made using α -gallium oxide and zirconia by fabricating three types of discs: (a) 50 vol.% α -gallium oxide + 50 vol.% 8YSZ, (b) 70 vol.% α -gallium oxide + 30 vol.% 8YSZ, and (c) 50 vol.% α -gallium oxide + 50 vol.% 4.5YSZ. Disc-shaped samples of 2.5 mm thickness of compositions (a), (b), and (c) are fabricated using requisite powder mixtures, die-pressing, followed by isostatic pressing, and then sintering in air at 1600°C. The discs after sintering are placed in a powder mixture containing Na_2O and Li_2O as in Example I.. The discs are maintained at 1450°C for 16 hours to form sodium- β "-gallate. Potassium- β "-gallate is formed in a similar manner using a powder mixture containing K_2O instead of Na_2O .

Comparative Example

Flat membranes or tubes of α - Al_2O_3 made by sintering α - Al_2O_3 at 1600°C for 25 2 hours were placed inside a zirconia crucible in which was placed a mixture of Na- β "-alumina powder with some excess Na_2O . A lid was placed over the crucible and it was heated to a temperature between 1300 and 1450°C, for 1 to 16 hours. The converted thickness squared vs. time is shown in Figure 9. The activation energy of the conversion process was determined to be 267 kJ/mol. Using this process α -alumina sheets of 75 μm thickness can be converted into β "-alumina in 16 hours at

1450°C. Ionic conductivity tests, chemical analysis, and photo micrographs were made and the results were consistent with known properties of Na- β'' -alumina.

Referring to both Figures 3 and 9, that the present process when compared with the prior-art diffusion process achieves conversion thicknesses that are orders of magnitude greater for the same time. It is worth-noting from Figures 3 and 9, that for samples (a), (b), and (c) of the invention, the thickness of converted material, X, varied linearly with time. By contrast, in the case of the comparative sample, the thickness squared is linear with time, indicative of kinetics dictated by diffusion. In Figure 3 is also shown a plot of a prior-art comparative sample (d) of pure α -alumina heat treated for various times up 16 hours at 1450°C. The converted region after 16 hours was only 65 μm thick. This contrasted with samples according to the present invention where the region converted into sodium- β'' -alumina under similar conditions was in excess of 1500 μm (1.5 mm). This is because in the comparative sample, the kinetics were limited by slow diffusion of oxygen through Na- β'' -alumina.

While this invention has been described with reference to certain specific embodiments and examples, it will be recognized by those skilled in the art that many variations are possible without departing from the scope and spirit of this invention, and that the invention, as described by the claims, is intended to cover all changes and modifications of the invention which do not depart from the spirit of the invention.

CLAIMS

What is claimed is:

1. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic; forming a shaped composite of a precursor ceramic of $\alpha\text{-Al}_2\text{O}_3$, or Ga_2O_3 , or mixtures thereof, and the oxygen-ion conducting ceramic such that a continuous matrix exists in the composite for both the precursor ceramic and oxygen-ion conductor, subjecting the composite to a vapor containing the metal oxide of an alkali metal at sufficient temperature and for sufficient time to convert the precursor ceramic to an alkali-metal-ion conducting ceramic of alkali-metal- β - or $\beta''\text{-X}_2\text{O}_3$, where X is Al or Ga.
2. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 1 wherein the precursor ceramic comprises $\alpha\text{-Al}_2\text{O}_3$ and the precursor ceramic is converted into alkali-metal- β - or $\beta''\text{-Al}_2\text{O}_3$.
3. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 1 wherein the precursor ceramic comprises Ga_2O_3 and the precursor ceramic is converted into alkali-metal- β - or $\beta''\text{-Ga}_2\text{O}_3$.
4. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 1 wherein the precursor ceramic comprises a mixture of $\alpha\text{-Al}_2\text{O}_3$ and Ga_2O_3 , the precursor ceramic is converted into a mixture alkali-metal- β - or $\beta''\text{-Al}_2\text{O}_3$ and alkali-metal- β - or $\beta''\text{-Ga}_2\text{O}_3$.
5. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 4 wherein the mixture alkali-metal- β - or $\beta''\text{-Al}_2\text{O}_3$ and alkali-metal- β - or $\beta''\text{-Ga}_2\text{O}_3$ is a solution of alkali-metal- β - or $\beta''\text{-Al}_2\text{O}_3$ and alkali-metal- β - or $\beta''\text{-Ga}_2\text{O}_3$.

6. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 1 wherein the composite is subjected to a temperature greater than about 800°C.

7. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 1 wherein the alkali metal is chosen from the group consisting of lithium, sodium, potassium, rubidium, and cesium.

8. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 1 wherein the alkali metal is chosen from the group consisting of sodium, and potassium.

9. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 1 wherein the conversion of the precursor is in the presence of a stabilizer and the precursor ceramic is converted to alkali-metal- β'' -alumina, or alkali-metal- β'' -gallate, or mixtures thereof.

10. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal-ion conducting ceramic as in Claim 9 wherein the stabilizer is chosen from the group consisting of MgO, Li₂O, and ZnO.

11. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina that comprises; forming a shaped composite of α -alumina and the oxygen-ion conducting ceramic such that a continuous matrix exists in the composite for both the α -alumina and oxygen-ion conductor, subjecting the composite to a vapor containing the metal oxide of an alkali metal at sufficient temperature and for sufficient time to convert the α -alumina to alkali-metal- β - or β'' -alumina.

12. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the composite is subjected to a temperature greater than about 800°C.
13. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the composite is subjected to a temperature between about 1200°C and 1500°C.
14. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the shaped composite of α -alumina and the oxygen-ion conductor is embedded in a powder that releases the vapor containing the alkali-metal oxide at the temperature to which the shaped composite of α -alumina and the oxygen-ion conductor is subjected.
15. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the alkali metal is chosen from the group consisting of lithium, sodium, potassium, rubidium, and cesium.
16. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the alkali metal is chosen from the group consisting of sodium, and potassium.
17. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the alkali metal is sodium, the vapor contains an oxide of sodium, and the α -alumina is converted to sodium β - or β'' -alumina.
18. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the alkali metal is potassium, the vapor contains an oxide of potassium, and the α -alumina is converted to potassium β - or β'' -alumina.

19. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the vapor also contains a stabilizer and the α -alumina is converted to alkali-metal- β'' -alumina.

20. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 19 wherein the stabilizer is chosen from the group consisting of MgO, Li₂O, and ZnO.

21. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 19 wherein the alkali metal is sodium, the alkali-metal oxide in the vapor is an oxide of sodium, and the α -alumina is converted to sodium β'' -alumina.

22. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 19 wherein the shaped composite of α -alumina and the oxygen-ion conductor is embedded in a powder that releases the vapor containing the alkali-metal oxide and the stabilizer at the temperature to which the shaped composite of α -alumina and the oxygen-ion conductor is subjected.

23. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the shaped composite of α -alumina and the oxygen-ion conductor is also formed with a stabilizer and the α -alumina is converted to alkali-metal- β'' -alumina.

24. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 23 wherein the stabilizer is chosen from the group consisting of MgO, Li₂O, and ZnO.

25. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the oxygen-ion conductor comprises a ceramic containing one or more members chosen from the group consisting of zirconia, ceria, hafnia, and thoria.

26. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina as in Claim 11 wherein the oxygen-ion conductor comprises a ceramic chosen from the group consisting of yttria stabilized zirconia, rare-earth-oxide-doped zirconia, and scandia-doped zirconia, rare-earth doped ceria and alkaline-earth doped ceria, stabilized hafnia, and thoria.

27. A process for forming ceramic composites of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -gallate that comprises; forming a shaped composite of α -gallium oxide and the oxygen-ion conductor such that a continuous matrix exists in the composite for both the α -gallium oxide and oxygen-ion conductor, subjecting the composite to a vapor containing the metal oxide of an alkali metal at sufficient temperature and for sufficient time to convert the α -gallium oxide to alkali-metal- β - or β'' -gallate.

28. A process for forming a ceramic composite of an oxygen-ion conducting ceramic and an alkali-metal- β - or β'' -alumina or gallate comprising converting a precursor ceramic of α -alumina, gallium oxide, or mixtures thereof, to an alkali-metal- β - or β'' -phase by exposing an alkali-metal oxide containing vapor to a composite comprising continuous phases of the precursor ceramic and the oxygen-ion conducting ceramic at a temperature sufficient to diffuse alkali metal ions through alkali-metal- β - or β'' -phase converted from precursor ceramic and oxygen ions through the oxygen-ion conducting ceramic to a reaction front where precursor ceramic is converted to the alkali-metal- β - or β'' -phase comprising alkali-metal- β - or β'' -alumina, alkali-metal- β - or β'' -gallate, or mixtures thereof.

29. A ceramic composite comprising a continuous phase of an alkali-metal-ion conductor and a continuous phase of a ceramic oxygen-ion conductor, the alkali-metal-ion conductor chosen from the group consisting of alkali-metal- β - or β'' -alumina, alkali-metal- β - or β'' -gallate, or mixtures thereof.

30. A ceramic composite as in Claim 29 wherein the alkali-metal-ion conductor is lithium-, sodium-, potassium-, rubidium- or cesium- β - or β'' -alumina.

31. A ceramic composite as in Claim 29 wherein the alkali-metal- β - or β'' -alumina is sodium- or potassium- β'' -alumina.

32. A ceramic composite as in Claim 29 wherein the alkali-metal- β - or β'' -alumina is sodium- β'' -alumina.

33. A ceramic composite as in Claim 29 wherein the ceramic oxygen-ion conductor comprises a ceramic containing one or more members chosen from the group consisting of zirconia, ceria, hafnia, and thoria.

34. A ceramic composite comprising a continuous phase comprising alkali-metal- β - or β'' -alumina and a continuous phase of a ceramic oxygen-ion conductor.

35. A ceramic composite as in Claim 34 wherein the alkali-metal- β - or β'' -alumina is lithium-, sodium-, potassium-, rubidium- or cesium- β - or β'' -alumina.

36. A ceramic composite as in Claim 34 wherein the alkali-metal- β - or β'' -alumina is sodium- or potassium- β'' -alumina.

37. A ceramic composite as in Claim 34 wherein the alkali-metal- β - or β'' -alumina is sodium- β'' -alumina.

38. A ceramic composite as in Claim 34 wherein the ceramic oxygen-ion conductor comprises a ceramic containing one or more members chosen from the group consisting of zirconia, ceria, hafnia, and thoria.

39. A ceramic composite as in Claim 34 wherein the ceramic oxygen-ion conductor comprises a ceramic chosen from the group consisting of yttria stabilized

zirconia, rare-earth-oxide-doped zirconia, and scandia-doped zirconia, rare-earth doped ceria and alkaline-earth doped ceria, stabilized hafnia, and thoria.

40. A ceramic composite comprising a continuous phase comprising alkali-metal- β - or β'' -gallate and a continuous phase of a ceramic oxygen-ion conductor.

41. A ceramic composite comprising a continuous phase of a mixture of alkali-metal- β - or β'' -alumina and of alkali-metal- β - or β'' -gallate, and a continuous phase of a ceramic oxygen-ion conductor.

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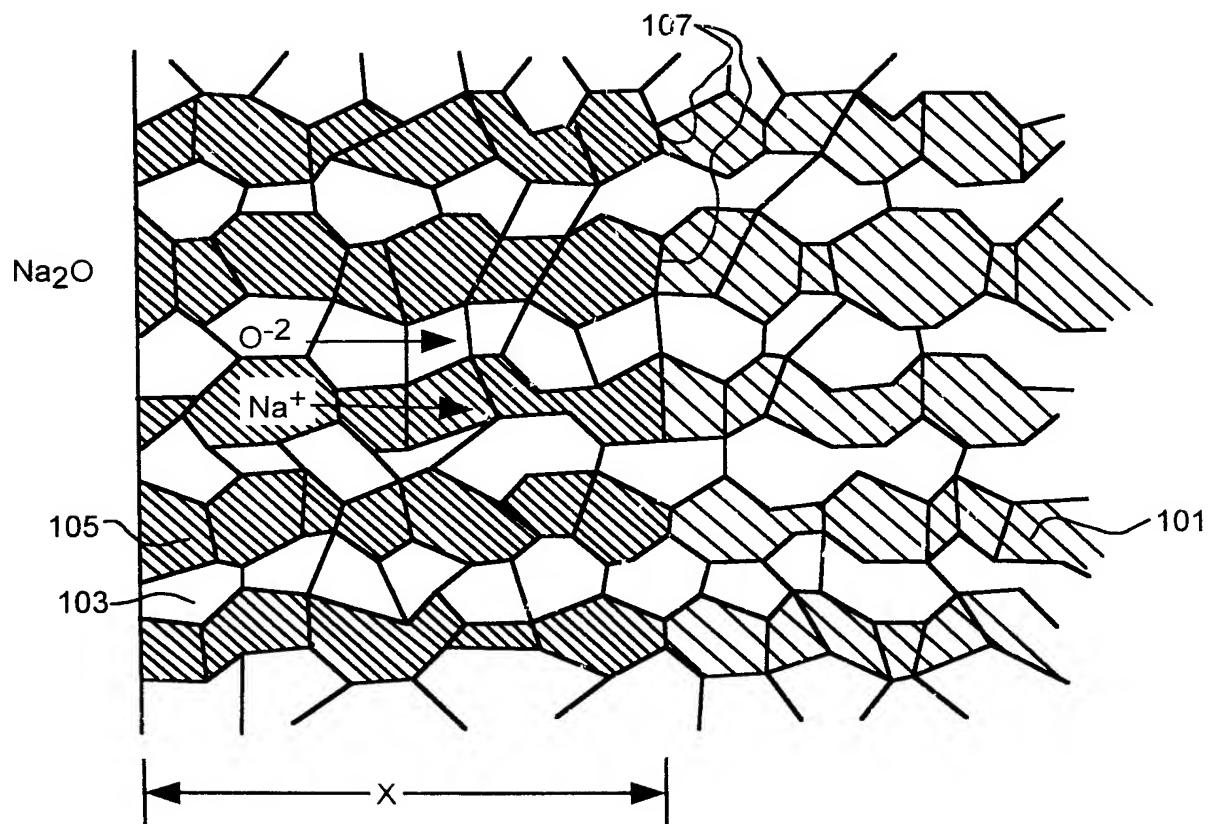


Fig. 1

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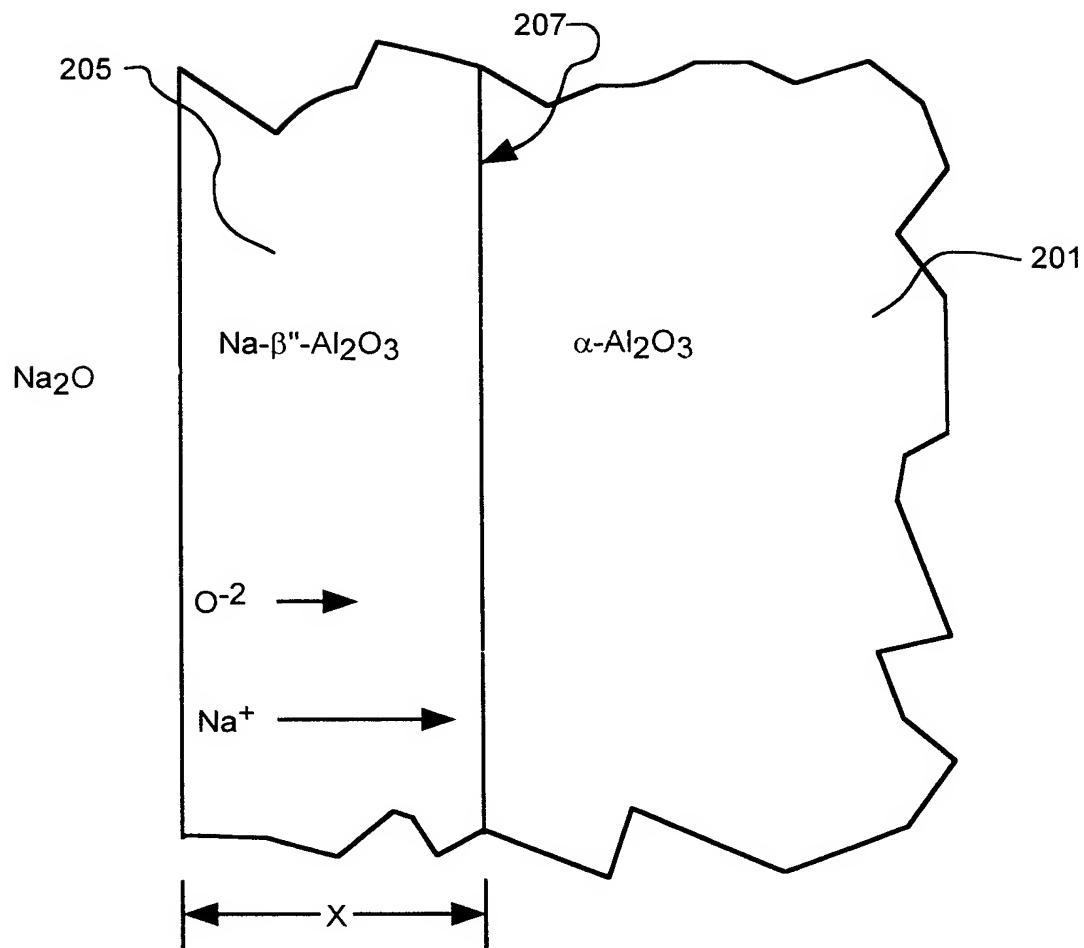


Fig. 2
PRIOR-ART

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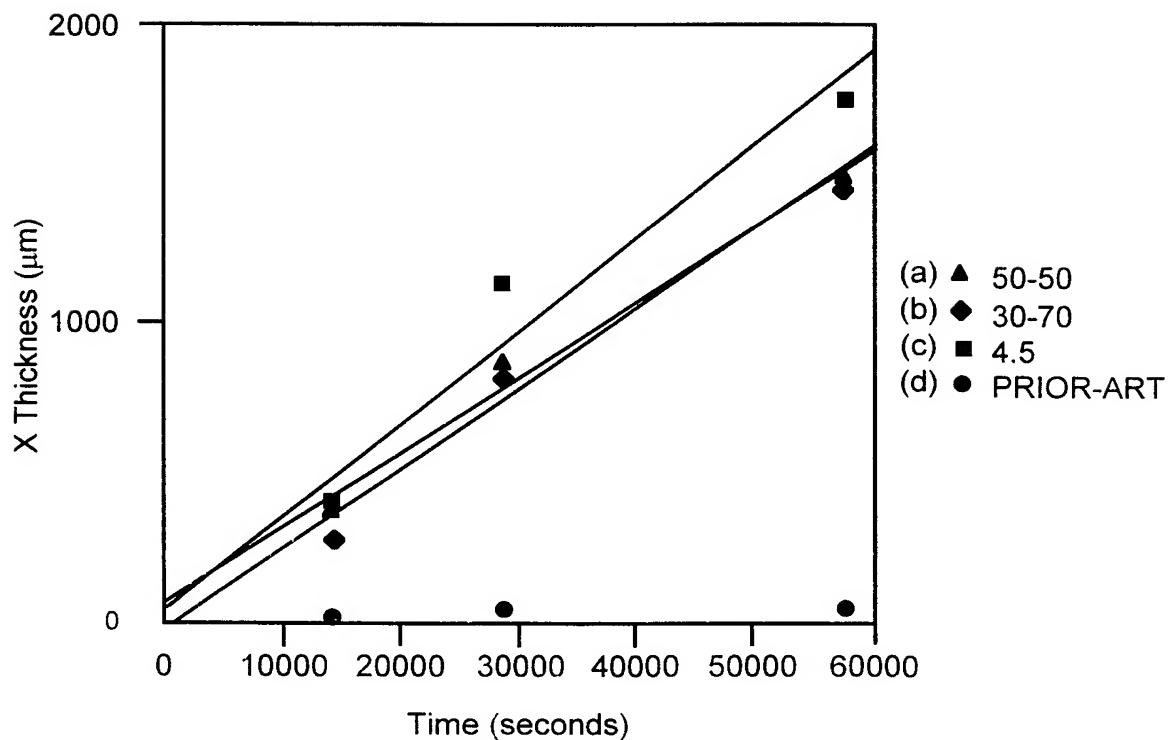


Fig. 3



Fig. 4

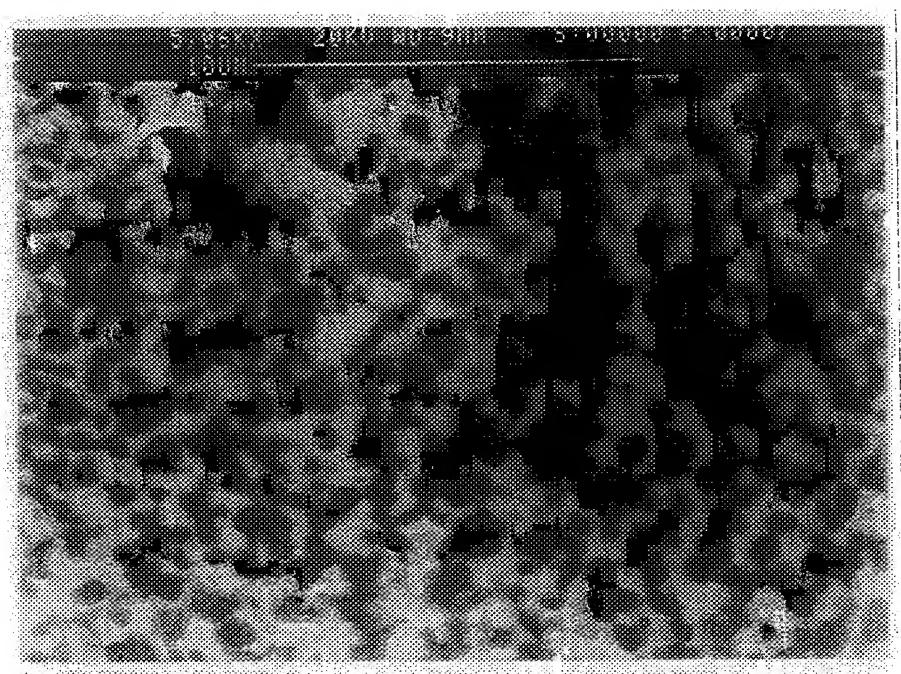


Fig. 5A

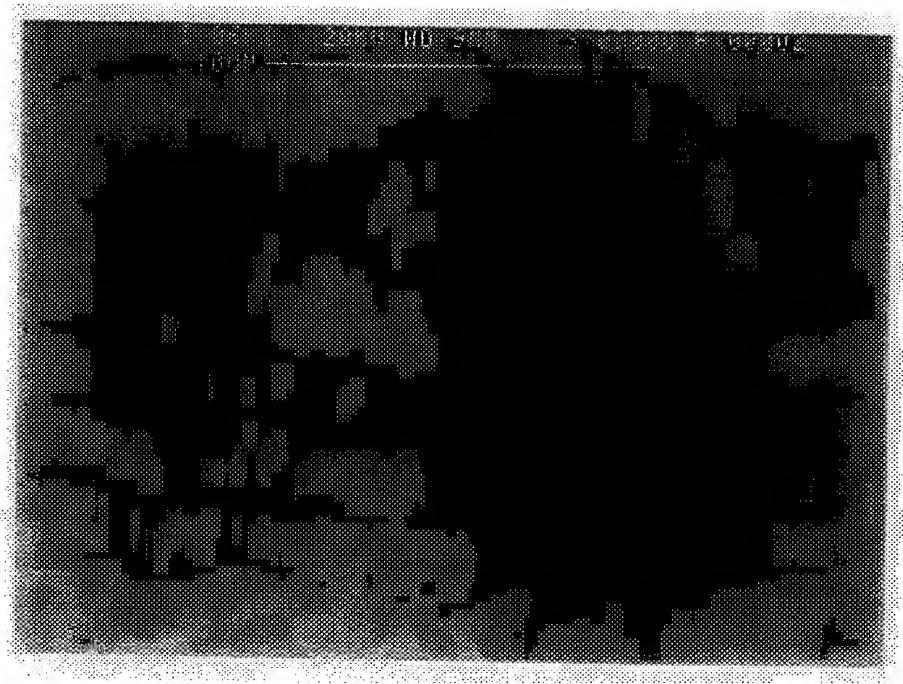


Fig. 5B

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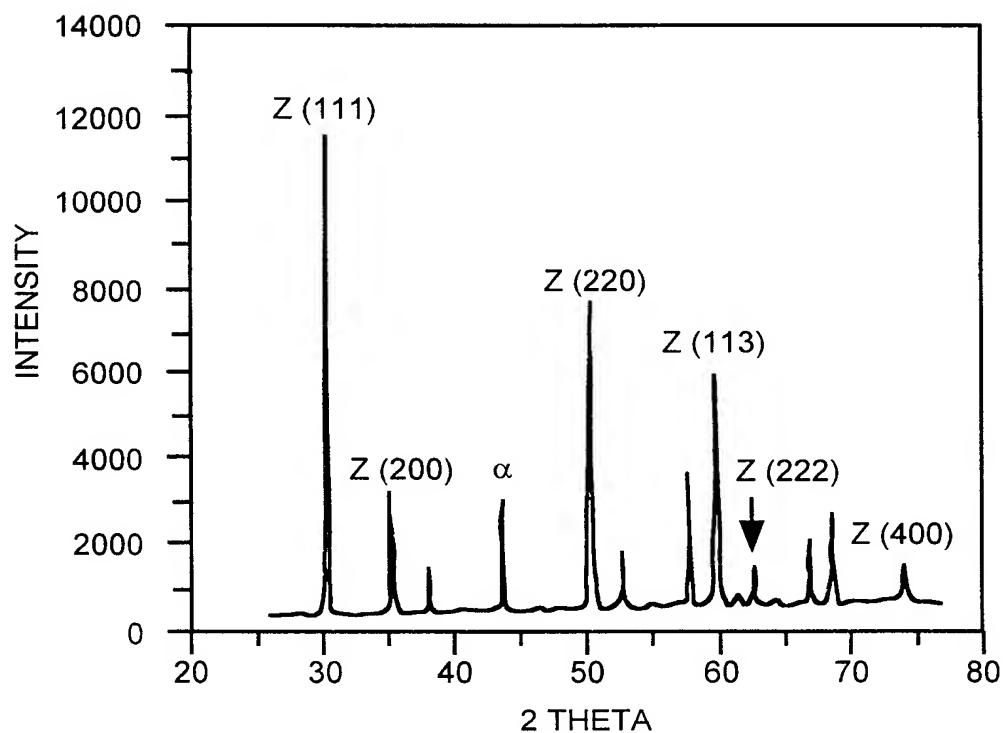


Fig. 6

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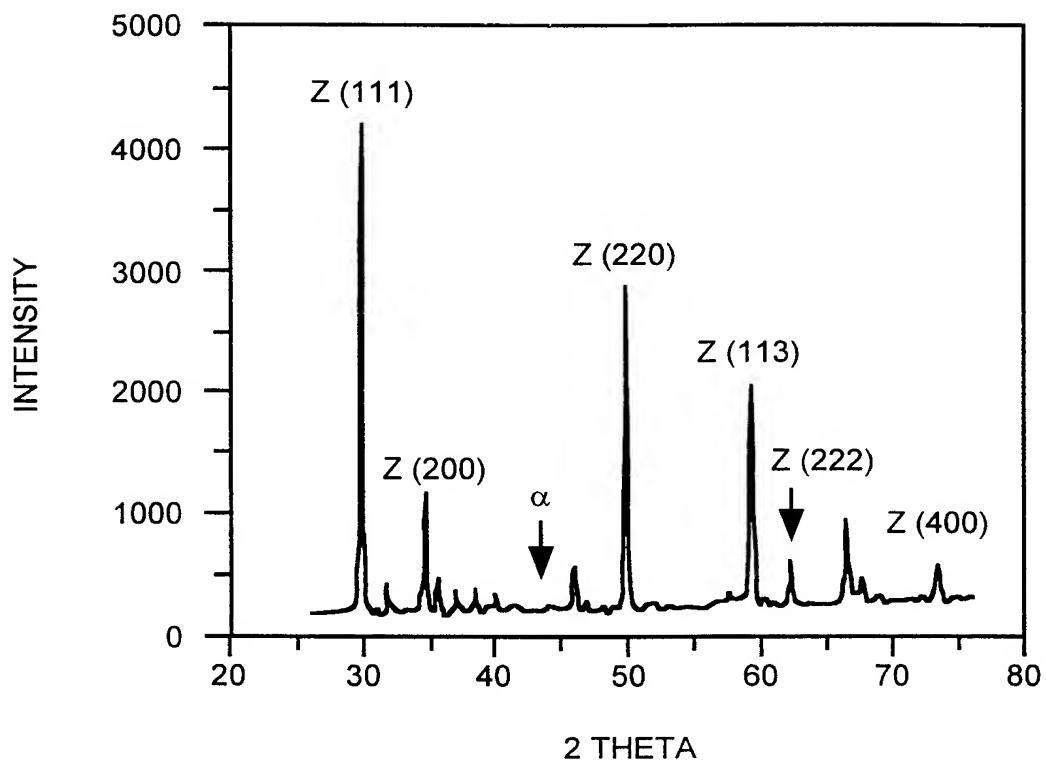


Fig. 7

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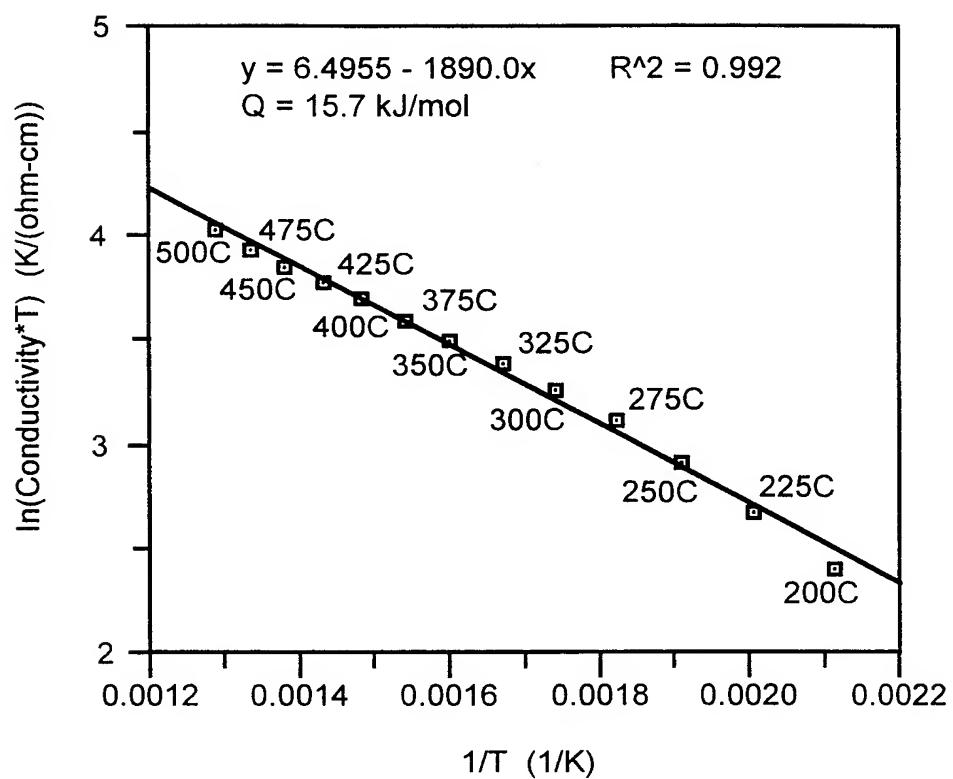
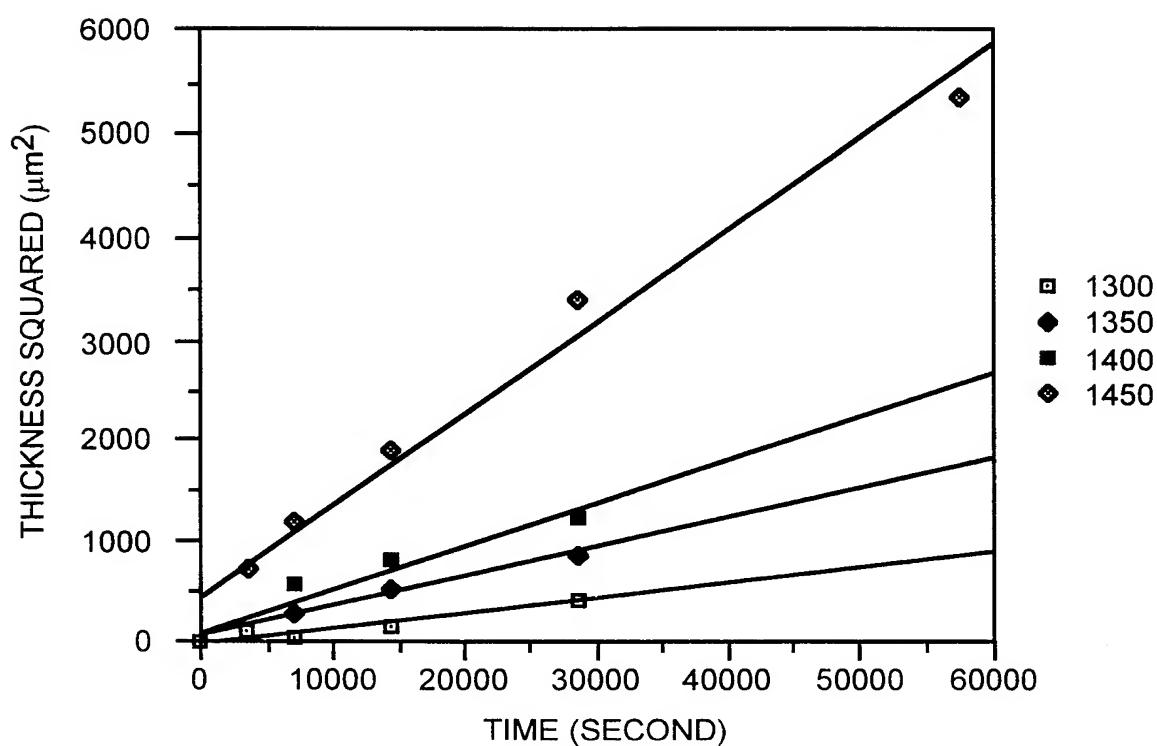


Fig. 8

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PRIOR-ART

FIG. 9

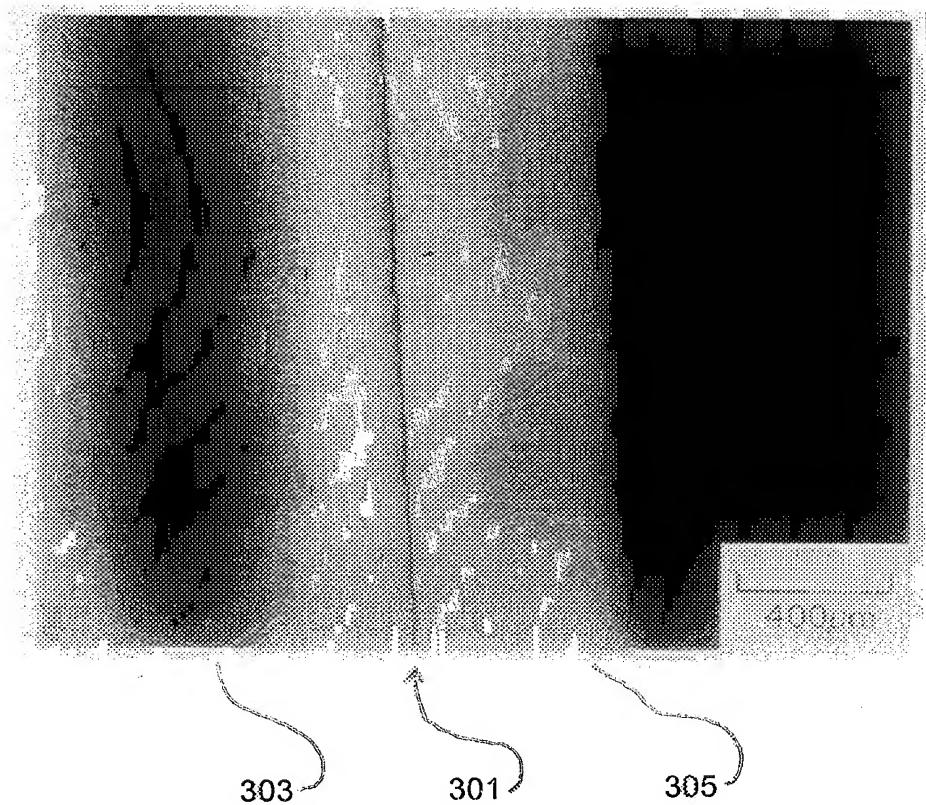


Fig. 10

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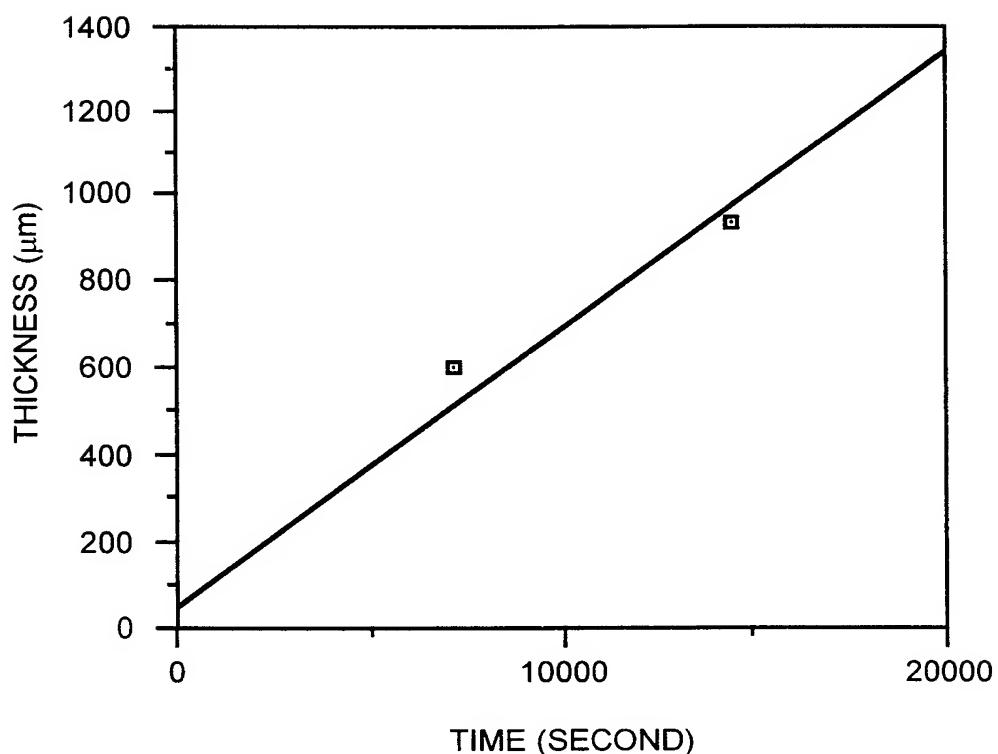


Fig. 11

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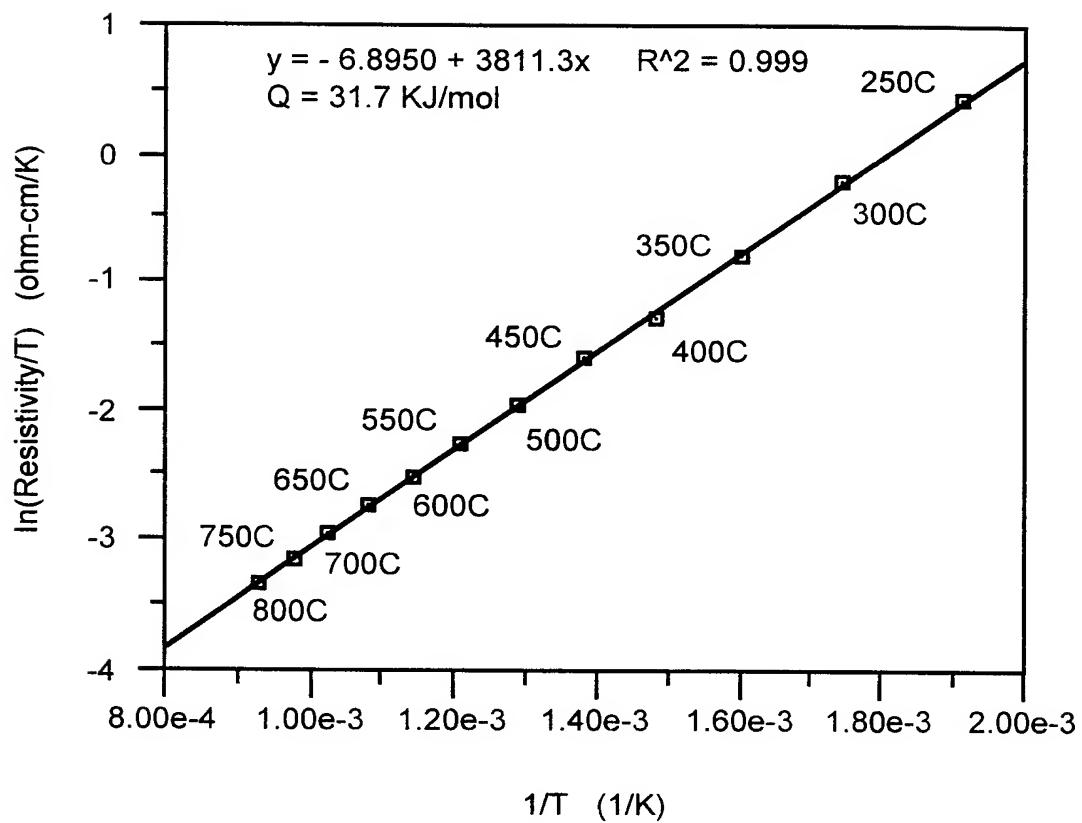


Fig. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/27859

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C04B 35/01, 35/10, 35/48; B32B 18/00; H01M 6/18
US CL :501/105, 119, 127, 153; 264/82, 681; 428/689, 697; 429/193

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/105, 119, 127, 153; 264/82, 681; 428/689, 697; 429/193
IPC(6): C04B 35/01, 35/10, 35/48

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,263,381 A (McENTIRE ET AL.) 21 April 1981 (21/04/81), see entire document.	1-41
A	US 5,415,127 A (NICHOLSON ET AL.) 16 May 1995 (16/05/95), see entire document.	1-41
A -- Y	US 5,137,853 A (ICHIKAWA ET AL.) 11 August 1992 (11/08/92), see the claims.	1-28,39-41 ----- 29-38
A -- Y	US 3,707,589 A (CHIKU ET AL.) 26 December 1972 (26/12/72), see column 4, lines 5-10 and the claims.	1-28, 39-41 ----- 29-38
A	US 4,294,898 A (HARTSTEIN) 13 October 1981 (13/10/81), see entire document.	1-41

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance		
E earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

18 MARCH 1999

Date of mailing of the international search report

12 APR 1999

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